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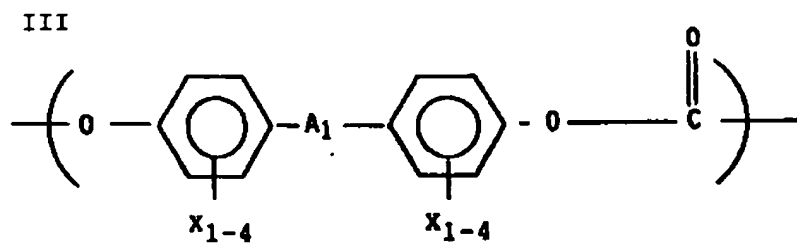
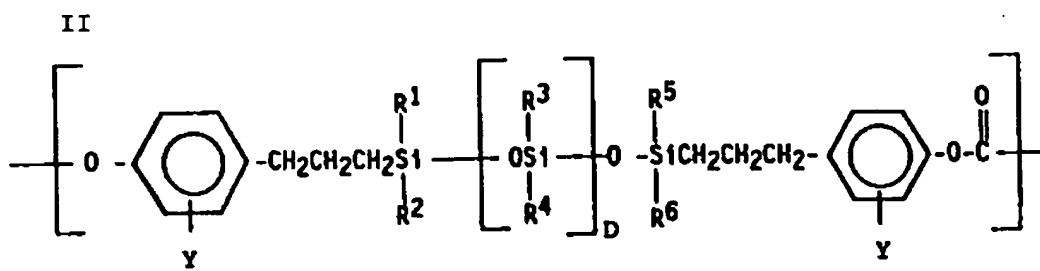
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EUROPEAN PATENT APPLICATION(21) Application number: **93116593.0**(61) Int. Cl.⁵: **C08L 69/00, C08L 83/10,
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12/13 Essex Street
London WC2R 3AA (GB)(54) **Polymer blend containing aromatic polycarbonate, styrene polymer and a polysiloxane polycarbonate block copolymer.**

(57) The invention relates to a polymer mixture which comprises an aromatic polycarbonate, a styrene-containing copolymer and/or a styrene-containing graft polymer and a given type of polysiloxane-polycarbonate block copolymer. It has been found that the use of this given type of polysiloxane-polycarbonate block copolymer leads to a polymer mixture having improved impact strength properties. The polysiloxane-polycarbonate block copolymer used is built up from

(a) 1-50% by weight of polysiloxane blocks of formula II and

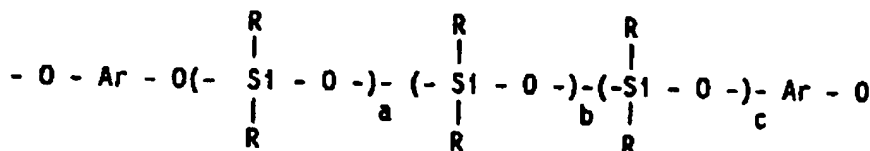
(b) 50-99% by weight of polycarbonate blocks of formula III, wherein R_1 , R_2 , R_3 , R_4 , R_5 and R_6 each independently of each other represent a hydrogen atom, a hydrocarbyl or a halogenated hydrocarbyl, D is an integer from 5-140, Y is a hydrogen atom or an alkoxy, and wherein A is a bivalent hydrocarbon group having 1-15 carbon atoms, which bivalent hydrocarbon group may be substituted, is an -S-; an -S-S-; an -S(O)-; an -S(O)₂-; an -O-, or a -C- and each X independently of each other is a hydrogen atom, a halogen or a monovalent hydrocarbon (see Figures).**EP 0 600 196 A1**



The invention relates to a polymer mixture which comprises an aromatic polycarbonate without polysiloxane blocks (A), a styrene-containing copolymer and/or a styrene-containing graft polymer (B) and a polysiloxane-polycarbonate block copolymer (C).

Polymer mixtures which comprise an aromatic polycarbonate, a styrene-containing graft polymer, for example, ABS and a polysiloxane-polycarbonate block copolymer are disclosed in EP-A-0135794. According to this prior art a polysiloxane-polycarbonate block copolymer is used which comprises polysiloxane blocks of formula (I)

(I)



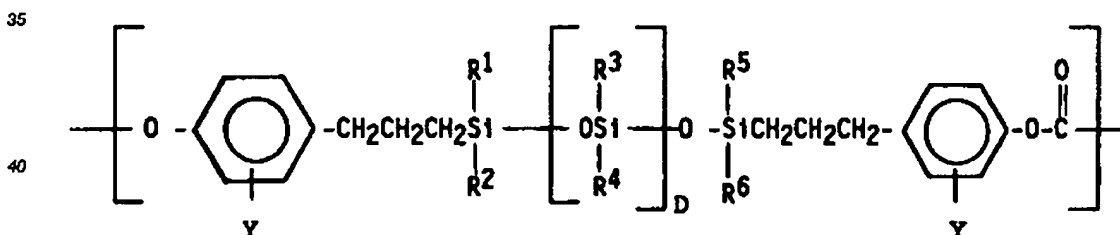
In this formula I, Ar is an arylene radical obtained from a diphenol. According to EP-A-0135794 block copolymers are used which comprise 2.5-25% by weight of polysiloxane blocks of formula I and 97.5-75% by weight of blocks having a polycarbonate structure. When the polymer mixture according to EP-A-0135794 comprises a mixture of a polysiloxane-polycarbonate block copolymer and a polycarbonate without polysiloxane blocks, the content of polysiloxane blocks in this mixture must be between 2.5 and 25% by weight.

25 The invention is based on the discovery that polymer mixtures having improved properties can be obtained by using certain polysiloxane-polycarbonate block copolymers. More in particular, polymer mixtures having a better impact strength can be obtained in this manner.

In the polymer mixture according to the invention a polysiloxane-polycarbonate block copolymer is used which is built up from

30 (a) 1-50% by weight of polysiloxane blocks of formula (II)

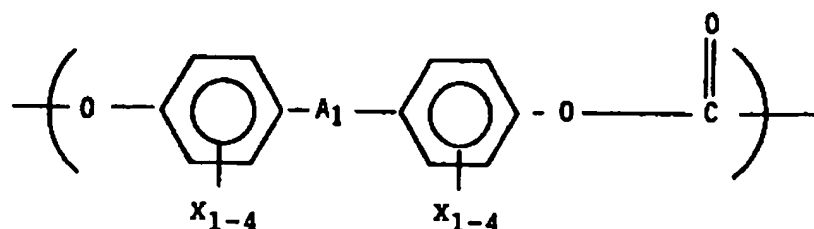
(II)



45 and

(b) 50-99% by weight of polycarbonate blocks of formula (111)

(III)



wherein R₁, R₂, R₃, R₄, R₅ and R₆ in formulae II and III each independently of each other represent a

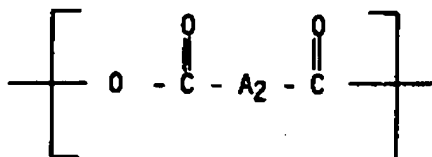
hydrogen atom, a hydrocarbyl or a halogenated hydrocarbyl, D is an integer from 5 to 140, Y is a hydrogen atom or an alkoxy, and wherein Al is a bivalent hydrocarbon group having 1-15 carbon atoms, which bivalent hydrocarbon group may be substituted, is an -S-; an -S-S-; an -S(O)-; an -S(O)₂-; an -O-, or a -C- and every X independently of each other is a hydrogen atom, a halogen or a monovalent hydrocarbon.

It is possible to use in the polymer mixture according to the invention polysiloxane-polycarbonate block copolymers of the type just mentioned with polycarbonate blocks which are built up for 75-99% by weight from units of the above-mentioned formula III

and for

1-25% by weight from aliphatic diester units of formula (IV):

(IV)



wherein A₂ is an alkylene radical having 6-18 carbon atoms and Al and X have the meanings given hereinbefore.

The polymer mixture according to the invention is preferably composed so that, per 100 parts by weight of constituent A plus constituent B plus constituent C, it is built up from

- 50-90% by weight, more preferably 60-80% by weight of constituent A and
- 2-40% by weight, more preferably 5-20% by weight of constituent B and
- 2-40% by weight, more preferably 5-20% by weight of constituent C,

constituent B comprising 50-100% by weight of the graft copolymer and 0-50% by weight of the copolymer.

It is preferable for the content of polysiloxane units in constituent C plus the content of rubber-like graft base in constituent B together, calculated with respect to the overall quantity by weight of the constituents A plus B plus C, to be between 2.5 and 25% by weight.

As a styrene-containing graft polymer having a rubber-like graft base is preferably used in the polymer mixture according to the invention a graft polymer obtained by grafting a mixture of (1) styrene and/or alpha-methyl styrene and/or a styrene substituted in the aromatic nucleus and (2) a methacrylonitrile and/or acrylonitrile and/or maleic acid anhydride and/or derivative of maleic acid anhydride and/or acrylic monomer, on a rubber (3).

As a styrene-containing copolymer, the polymer mixture according to the invention may comprise a copolymer which is built up from (1) styrene, and/or alpha-methyl styrene and/or a styrene substituted in the aromatic nucleus and (2) a methacrylonitrile and/or acrylonitrile and/or maleic acid anhydride and/or derivative of maleic acid anhydride and/or acrylic monomer.

The polymer mixture according to the invention may comprise a mixture of a styrene copolymer and a styrene graft polymer as described hereinbefore.

The invention also relates to articles formed from the polymer mixture according to the invention.

The polymer mixture according to the invention comprises at any rate the following constituents:

- A. an aromatic polycarbonate, and
- B. a styrene-containing copolymer and/or a styrene-containing graft polymer, and
- C. a polysiloxane-polycarbonate block copolymer.

The polymer mixture according to the invention may moreover comprise one or more of the following constituents:

- D. flame-retardants
- E. conventionally used additives.

A. Aromatic polycarbonates without polysilixane blocks

Aromatic polycarbonates are materials known per se. They are generally prepared by reacting a dihydric phenol compound with a carbonate precursor, for example, phosgene, a halogen formate or a carbonate ester. Aromatic polycarbonates are polymers which comprise units of formula (V)



wherein A_3 is a bivalent aromatic radical which is derived from the dihydric phenol which has been used in the preparation of the polymer. Mononuclear or polynuclear aromatic compounds which comprise two hydroxy radicals each directly bonded to a carbon atom of an aromatic nucleus may be used as dihydric phenols in the preparation of the aromatic polycarbonates.

The branched polycarbonates known per se as described, for example, in US-A-4,001,184 are also suitable.

The so-called polyester carbonates which are obtained by performing the polymerisation reaction in the presence of an ester precursor, for example, a difunctional carboxylic acid, for example, terephthalic acid or an ester-forming derivative thereof, are also suitable aromatic polycarbonates. These polyester carbonates have ester compounds and carbonate compounds in the polymeric chain. Polyester carbonates are described, for example, in US-A-3,169,121.

It is also possible to use a mixture of different polycarbonates.

20 B. Styrene-containing copolymer and/or a styrene-containing graft polymer having a rubber-like graft base

Suitable styrene-containing copolymers and suitable styrene-containing graft polymers are described, for example, in EP-A-0174493 and in EP-A-0135794.

25 Styrene-containing copolymers are copolymers built up from units derived from (1) styrene, and/or alpha-methyl styrene and/or styrene compounds substituted in the aromatic nucleus and (2) acrylonitrile and/or methacrylonitrile and/or maleic acid anhydride and/or a derivative of maleic acid anhydride and/or acrylic monomer. Suitable derivatives of maleic acid anhydride are maleimide and N-phenyl maleimide. Suitable acrylic monomers are, for example, methyl methacrylate, (meth)acrylic acid. These copolymers are known per se and they can be obtained according to conventionally used methods of preparing copolymers.

Styrene-containing graft polymers are obtained by grafting a mixture of at least two monomers on a rubber-like graft base. Suitable graft bases are, for example, poly-butadiene, butadiene-styrene copolymers. Other rubbers, for example, acrylate rubbers and EPDM rubbers may also be considered. A mixture of monomers is then grafted on the said rubbers. Suitable monomers are claimed in Claim 5.

35 C. Polysiloxane-polycarbonate block copolymers

The polymer mixture according to the invention comprises a polysiloxane-polycarbonate block copolymer as claimed in Claim 1 or Claim 2 of the present Patent Application. Block copolymers as claimed in Claim 1 and their mode of preparation are disclosed in EP-A-92305883, filed on June 25, 1992 and having a US priority date of July 1, 1991, filing number 724022.

Block copolymers as claimed in Claim 2 and their mode of preparation are disclosed in EP-A-92305886, filed on June 25, 1992 and having a US priority date of July 1, 1991, filing number 724018.

45 Polymer mixtures of polycarbonates and block copolymers as used in the invention are disclosed in EP-A-92305885, filed on June 25, 1992 and having a U.S. priority date of July 1, 1991, filing number 724,023.

All the polysiloxane-polycarbonate block copolymers described in the three Patent Applications mentioned hereinbefore may be used in the polymer mixture according to the invention.

50 E. Flame-retardants

The polymer mixture according to the invention may comprise one or more flame-retardants. All the conventionally used agents suitable to improve the flame-retarding properties of polycarbonate polymers and/or of styrene-containing copolymers or graft polymers may be considered. By way of example may be mentioned:

- a salt having flame-retarding properties for aromatic polycarbonates
- a halogen-containing low-molecular and/or high-molecular compound and/or

- a perfluoroalkane polymer and/or
- a metal compound active as a synergist
- poly(aryl-arylene phosphates) or poly(alkaryl-arylene phosphates) as described in EP-A-0363608.

Salts having flame-retarding properties are generally known and are used on a large scale in polymer mixtures which comprise a polycarbonate. All the salts which are suitable for polymer mixtures having a polycarbonate may be used in the polymer mixture according to the invention. In particular may be mentioned organic and inorganic sulphonates, for example, sodium trichlorobenzene-sulphonate, salts of sulphone sulphonates, for example, the potassium salt of diphenyl sulphone sulphonate, salts of perfluorinated alkane sulphonic acids and sodium aluminium hexafluoride.

Examples of suitable halogen-containing compounds are decabromodiphenyl ether, octabromodiphenyl ether and further oligomeric or polymeric bromine compounds, for example, derived from tetrabromobisphenol A or also poly-phenylene ethers brominated in the nucleus.

Tetrafluoroethylene polymers are preferably used as perfluoroalkane polymers. The polymer mixture according to the invention may further comprise a metal or metal compound active as a synergist, for example, antimony oxide and the like. These synergists are conventionally used in combination with halogen-containing compounds.

E. Conventionally used additives

In addition to the constituents mentioned hereinbefore the polymer mixture according to the invention may comprise one or more conventionally used additives, for example, fillers, reinforcing fibres, stabilisers, pigments and dyes, plasticisers, mould-release agents and antistatically active agents.

The polymer mixture may be obtained according to the conventionally used methods of preparing polymer mixtures, for example, by compounding the said constituents in an extruder.

The polymer mixture according to the invention may comprise

D. 0-20 parts by weight of one or more agents to improve the flame-retarding properties and/or

E. 0-100 parts by weight of conventionally used additives

per 100 parts by weight of A + B + C.

Comparative examples A to F; examples I to VIII.

In the following examples A, I, II and III the following constituents were used:

- PC-1 : an aromatic polycarbonate homopolymer derived from bisphenol A and phosgene without polysiloxane blocks having a weight-averaged molecular weight of 25,500.
- PC-2 : an aromatic polycarbonate homopolymer derived from bisphenol A and phosgene without polysiloxane blocks having a weight-averaged molecular weight of 28,000.
- ABS : A graft copolymer, built up substantially from a butadiene rubber on which styrene and acrylonitrile have been grafted, having a rubber content of approximately 50% by weight.
- SAN-1: A styrene-acrylonitrile copolymer having a weight-ratio styrene:acrylonitrile of 72 : 28 and having a weight-averaged molecular weight of 100,000.
- SAN-2: A styrene-acrylonitrile copolymer having a weight ratio styrene: acrylonitrile of 72 : 28 and having a weight-averaged molecular weight of 130,000.
- LR : A polysiloxane-polycarbonate block copolymer having 43% by weight of polysiloxane blocks of formula I (see above) and having 57% by weight of polycarbonate blocks of formula III. All R's in formula I represent a methyl group; Ar is an arylene group derived from bisphenol A, and the sum of a + b + c is on an average 10.
- The weight-averaged molecular weight of LR is approximately 60,000.
- XT-1: A polysiloxane-polycarbonate block polymer having 43% by weight of polysiloxane blocks of formula II (see above) and having 57% by weight of polycarbonate blocks of formula III. (see above).
- R₁ and R₂ all represent a methyl group, D is on an average 10 and Y is a hydrogen atom. Al in formula III represents a 2,2-propyl group and X is a hydrogen atom.
- The weight-averaged molecular weight of XT-1 is approximately 50,000.
- XT-2: A polysiloxane-polycarbonate block polymer having 20 by weight of polysiloxane blocks of formula II (see above) and having 80% by weight of polycarbonate blocks of formula III (see above).
- R₁ and R₂ all represent a methyl group, D is on an average 50 and Y is a hydrogen atom. A in formula III is a 2,2-propyl group and X is a hydrogen atom.

The weight-averaged molecular weight of XT-2 is approximately 30,000.

Various polymer mixtures were prepared from the constituents mentioned hereinbefore in the quantities recorded hereinafter in Tables A and B. The examples A to F relate to comparative prior art examples; the examples I to VIII relate to polymer mixtures according to the present invention. The various polymer mixtures were prepared by compounding the indicated constituents in an extruder. The resulting extrudate was then pelletised. Standardized test rods were injection-moulded from the pellets so as to determine the Izod notched impact strength at different temperatures (according to ASTM D 256) and to determine the notched impact strength according to the Charpy test (DIN 53453).

The melt viscosity index was also determined according to ISO 1133.

The results are recorded hereinafter in Tables A and B.

TABLE A

Example		A	B	C	I	II	III
Composition (parts by weight)							
Formulation No.		73	74	76	81	83	85
PC-1		60	55	58	48	55	58
SAN-1		22	22	22	22	22	22
ABS		18	18	10	10	18	10
LR		-	5	10	-	-	-
XT-1		-	-	-	-	5	10
XT-2		-	-	-	20	-	-
Rubber content (wt.%)		9.0	11.3	9.3	9.0	11.3	9.3
Properties							
MVI 260°C C/5 kg		12	16	80	19	12	14
Izod notched impact value	+23 °C	570	540	220	530	620	620
	-20 °C	390	270	50	520	500	490
	-48 °C	200	120	30	430	280	280
Charpy notched impact value	+23 °C	29	32	16	54	43	41
* rubber content: calculated from the polybutadiene content in the ABS and the polysiloxane content in LR, XT-1 or XT-2; expressed as a percentage by weight with respect to the polymer mixture.							

TABLE B

Example			D	E	F	IV	V	VI	VII	VIII
5	Composition (parts by weight)									
	Formulation No.		91	92	93	94	95	96	97	98
	PC-2		57	60	64	58	60	54	58	39
10	SAN-2		25	25	25	25	25	25	25	25
	ABS		18	10	6	-	10	10	6	-
	LR		-	5	5	17	-	-	-	-
15	XT-1		-	-	-	-	5	-	-	-
	XT-2		-	-	-	-	-	11	11	36
	Rubber content (wt.%)		9.0	7.2	5.2	7.2	7.2	7.2	5.2	7.2
20	Properties									
	MVI 260 C/5 kg		11	20	29	16	15	17	18	20
	Izod notched impact value	+ 23 ° C -20 ° C -40 ° C	570 480 280	480 150 150	510 150 80	540 470 370	620 530 210	670 600 170	650 560 190	480 890 570
25	Charpy notched impact value	+ 23 ° C	19	16	30	38	45	44	46	31
* Rubber content: see remark sub Table A										

It may be seen from Table A that the addition of a conventional polysiloxane-polycarbonate block copolymer (comparative examples B and C) leads to a considerable deterioration of the impact strength. This applies to the notched impact value according to Izod at all the indicated temperatures and to the notched impact value according to Charpy. The melt viscosity index also increases. Better notched impact values are nearly always obtained in the examples according to the invention (I, II and III), better than those determined in comparative example A without polysiloxane-polycarbonate block copolymer and at any rate always many times better than in the comparative examples B and C with the conventionally used polysiloxane-polycarbonate block copolymers. The melt viscosity index increases less strongly.

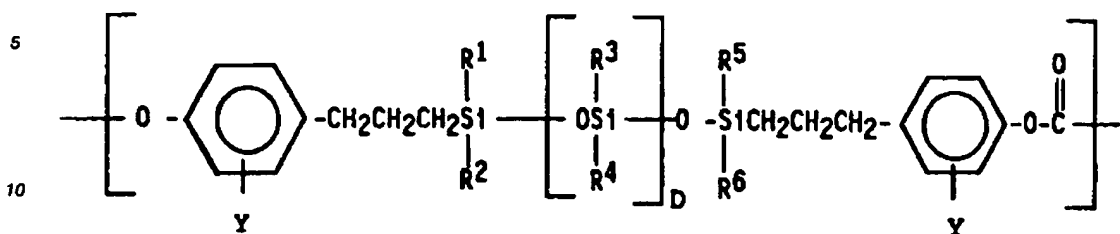
In the examples according to Table B another polycarbonate (with higher molecular weight) and another styrene-acrylonitrile copolymer (with higher molecular weight) were used. The results show a picture similar to that of Table A.

All the Patents and Patent Applications mentioned hereinbefore are deemed to be incorporated in the present Patent Application by reference.

Claims

1. A polymer mixture which comprises an aromatic polycarbonate without polysiloxane blocks (A), a styrene-containing copolymer and/or a styrene-containing graft polymer having a rubber-like graft base (B), and a polysiloxane-polycarbonate block copolymer (C), characterised in that the polymer mixture comprises a polysiloxane-polycarbonate block copolymer which is built up from (a) 1-50% by weight of polysiloxane blocks of formula (II)

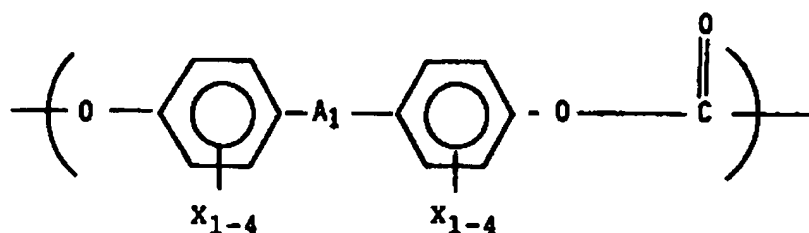
(II)



and

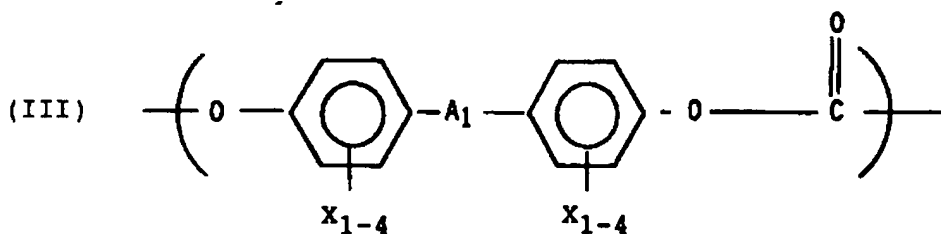
(b) 50-99% by weight of polycarbonate blocks of formula (III)

(III)

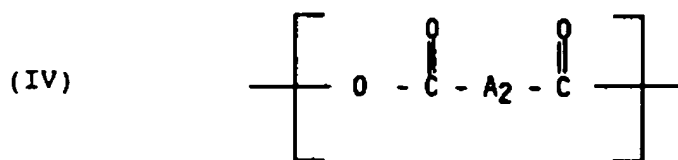


wherein formulae I and II R_1 , R_2 , R_3 , R_4 , R_5 and R_6 each independently of each other, represent a hydrogen atom, a hydrocarbyl or a halogenated hydrocarbyl, D is an integer from 5-140, Y is a hydrogen atom or an alkoxy, and wherein A_1 is a bivalent hydrocarbon group having 1-15 carbon atoms, which bivalent hydrocarbon group may be substituted, is an $-\text{S}-$; an $-\text{S}-\text{S}-$; an $-\text{S}(\text{O})-$; an $-\text{S}(\text{O})_2-$; an $-\text{O}-$, or a $-\text{C}-$, and every X , independently of each other, is a hydrogen atom, a halogen or a monovalent hydrocarbon.

2. Polymer mixture as claimed in Claim 1, characterised in that the polymer mixture comprises a polysiloxane-polycarbonate block copolymer (C), with polycarbonate blocks which are built up for 75-99% by weight from units of formula III



and for 1-25% by weight from aliphatic diester units of formula IV:



wherein A₂ is an alkylene radical having 6-18 carbon atoms and A₁, X have the meanings given hereinbefore.

3. Polymer mixture as claimed in Claim 1, characterised in that per 100 parts by weight of constituent A plus constituent B plus constituent C, the polymer mixture is built up from
 - 50-90% by weight of constituent A and
 - 2-40% by weight of constituent B and
 - 2-40% by weight of C, wherein
 constituent B consists of 50-100% by weight of the graft copolymer and 0-50% by weight of the copolymer.
4. Polymer mixture as claimed in Claim 1, characterised in that the content of polysiloxane units in constituent C plus the content of rubber-like graft base in constituent C together, calculated with respect to the overall quantity by weight of the constituents A plus B plus C, lies between 2.5 and 25% by weight.
5. Polymer mixture as claimed in Claim 1, characterised in that the polymer mixture comprises as constituent B a graft polymer obtained by grafting on a rubber (3) a mixture of (1) styrene and/or alpha-methyl styrene and/or a styrene substituted in the aromatic nucleus and (2) a methacrylonitrile and/or acrylonitrile and/or maleic acid anhydride and/or derivative of maleic acid anhydride and/or acrylic monomer.
6. Polymer mixture as claimed in Claim 1, characterised in that the polymer mixture comprises as constituent B a copolymer which is built up from units derived from (1) styrene, and/or alpha-methyl styrene and/or a styrene substituted in the aromatic nucleus and (2) a methacrylonitrile and/or acrylonitrile and/or maleic acid anhydride and/or derivative of maleic acid anhydride and/or acrylic monomer.
7. Polymer mixture as claimed in Claim 1, characterised in that the polymer mixture comprises as constituent B a mixture of a styrene copolymer and a styrene graft polymer.
8. Articles formed from the polymer mixture as claimed in Claim 1.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 93 11 6593

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CLS)
Y	EP-A-0 501 347 (MITSUBISHI GAS CHEMICAL COMP., INC.) * claims 1-3,9 * * page 3, line 33 - line 37 * * page 4, line 43 - line 58 * * examples 14,17,prep3 * ---	1,3-8	C08L69/00 C08L83/10 C08L25/02 C08L35/06 C08L55/02 C08L51/04
Y	DE-A-40 16 417 (BAYER AG) * claims 1,2 * * example 1 * ---	1,3-8	
D,P, A	EP-A-0 524 731 (GENERAL ELECTRIC COMP.) * claims 1-3 * ---	1,2	
A	PATENT ABSTRACTS OF JAPAN vol. 16, no. 126 (C-0923) 31 March 1992 & JP-A-03 292 359 (MITSUBISHI GAS CHEMICAL COMP., INC.) 24 December 1991 * abstract * ---	1,5-8	
A	WO-A-92 12208 (IDEMITSU PETROCHEMICAL CO.) & EP-A-0 517 927 * claims 1-3,6 * * page 3, line 49 - page 6, line 11 * * page 7, line 15 - page 8, line 7 * * page 8, line 52 - page 9, line 16 * ---	1,5-8	TECHNICAL FIELDS SEARCHED (Int.Cl.5) C08L C08G
D,A	EP-A-0 135 794 (BAYER AG) * claims 1,3,4 * * page 3, line 27 - page 6, line 6 * * page 8, line 14 - page 12, line 10 * * page 15 * ---	1,3,5-8	
A	EP-A-0 500 087 (CANON KABUSHIKI KAISHA) * abstract; example 5 * -----	1	
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 11 March 1994	Examiner Krische, D
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document			

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